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RESEARCH FOR THE AEROSPACE SYSTEMS DIRECTORATE (R4RQ)

Delivery Order 0006: Airbreathing Propulsion Fuels and Energy Exploratory Research and Development (APFEERD)

Subtask: Review of Materials Compatibility Tests of Synthesized Hydrocarbon Kerosenes And Blends

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Interim Report

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14. ABSTRACT

This report compares test data on the compatibility of elastomeric materials with synthesized hydrocarbon fuels and their blends with those of conventional Jet A/Jet A-1/JP-8 fuels to look for opportunities to safely reduce the amount of fit-for-purpose testing defined in ASTM D4054 in the approval process of synthesized kerosenes for use in jet fuel. The results of two studies are presented: (1) material properties of coatings, sealants, and O-rings at service temperatures, and (2) the effect of aromatics, natural and synthesized, on volume swell in these same materials. The results demonstrate that the responses of elastomers to kerosenes containing synthesized hydrocarbons are within the scope of responses to conventional jet fuels of similar aromatic content regardless of resource or processing. Also, the presence of cyclo-paraffins and tetralins plus indans do not affect the fundamental correlation with aromatic content at the concentrations used in the reported test programs.

15. SUBJECT TERMS
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Table of Contents

List of Figures

List of Tables

Acknowledgements

1.0 SUMMARY

Since 1997, close to 40 synthesized kerosenes and blends thereof with conventional jet fuel have been evaluated to determine if they are fit-for-purpose either as blending streams for making jet fuel or as fully synthetic jet fuels. As interest has grown in the use of renewable resources for producing jet fuel, there have been complaints from the producers about the time and cost of approving these products for use. Alternately, the Original Equipment Manufacturers (OEMs) have complained about the number of potential fuels and the time that the approval process is taking away from their primary function as an equipment manufacturer. This report compares test data on the compatibility of elastomeric materials with synthesized hydrocarbon fuels and their blends with those of conventional Jet A/Jet A-1/JP-8 fuels. The purpose is to look for opportunities to safely reduce the amount of fit-for-purpose testing defined in ASTM D4054 in the approval process of synthesized kerosenes for use in jet fuel. Such information could also increase the confidence in synthesized fuels in general, and ease the burden of reviewing the technical reports by the OEMs.

The test data reviewed herein focuses on the coatings, sealants, and O-rings which comprise the "short-short" list of non-metallic materials as developed jointly by the engine and airframe OEMs to identify potential problems. If no issues are identified, testing of the remainder of the materials identified in ASTM D4054 may be deferred upon the agreement of the OEMs. Two sets of tests are evaluated:

1. Tests conducted at temperature-time conditions specified in ASTM D4054 to determine if the materials met technical requirements of the product after fuel exposure at temperatures reflecting the environment of their use.
2. Tests at ambient temperature but with varying aromatic content to compare the response of the materials to synthesized aromatics and aromatics in conventional jet fuel.

The comparisons showed

1. Volume swell is considered to be the most sensitive to aromatic content
2. Nitrile materials are the most sensitive to aromatics
3. Sensitivity to aromatic content is linear with very little scatter
4. The test results with fuels containing synthesized aromatics were consistent with results using conventional jet fuel of similar aromatic content regardless of the concentration of cyclo-paraffins or tetralins and indans.

The major conclusions from this study are as follows:

- The responses of elastomers to kerosenes containing synthesized hydrocarbons are within the scope of responses to conventional jet fuels of similar aromatic content regardless of resource or processing.
- The presence of cyclo-paraffins and tetralins plus indans do not affect the fundamental correlation with aromatic content at the concentrations used in the reported test programs.

These results lay the groundwork for development of a generic Annex to D7566 that would define and control the use of certain synthesized kerosenes, with or without aromatics, regardless of resource or process.

2.0   INTRODUCTION

2.1   Background

Close to 40 synthesized kerosenes and blends thereof with conventional jet fuel have been evaluated over the last 16 years starting with the Sasol Iso-Paraffinic Kerosene (IPK), the first synthesized kerosene approved for use in commercial or military aviation under DEF STAN 91-91 Issue 3.[1] The restrictions place on the fuel were that it could be blended to a maximum of 50 vol% providing the aromatic content was greater than 8 vol%; all other fuel specifications for the final product had to be met, of course. The elements of the approval process were reviewed and refined a little for the approval of the Sasol Fully Synthetic Jet Fuel (FSJF) approved under DEF STAN 91-91 Issue 6 in February 2008.

In 2009, the approval protocol that had been used for the Sasol fuels was further refined and codified and then issued as ASTM D4054 *Standard Practice for Qualification and Approval of New Aviation Turbine Fuels and Fuel Additives*.[2] This protocol identifies the important properties and characteristics of jet fuels in the areas of:

- Chemistry
- Bulk physical and performance properties
- Electrical properties
- Ground handling and safety properties
- Compatibility with materials, additives, and other fuels

The protocol further provides guidance on values and limitations on these properties and characteristics for the candidate fuel to be considered "fit-for-purpose. Based on the results of these laboratory tests, the engine and airframe OEMs may then identify component and/or engine tests to confirm the candidate fuel, or its blend with conventional fuel, is "fit-for-purpose" as a jet fuel.

The blending and approval of the final fuel is defined in ASTM D7566 *Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons*.[3] Fuels that have gone through the D4054 approval process are defined in Annexes to D7566 according to their resources and processes. Annex 1 defining the use of Synthesized Paraffinic Kerosenes (SPK) from Fischer-Tropsch processes was included with the initial approval of D7566. It was another two years before SPKs processed from Hydrotreated Esters and Fatty Acids (HEFA) were approved in Annex 2; these fuels were identical to the fuels of Annex 1 in general chemistry and physical properties. Fuels from many other resources and processes have been introduced since then, but it was not until 2014 that a third Annex was approved using a lower concentration of only 10 vol%, necessitated by viscosity concerns. Annex 4 was approved in 2015 for the first synthesized fuel containing aromatics, and Annex 5 was approved in 2016 for a hydrocarbon product converted from an alcohol. At least a half-dozen other fuels/processes have been engaged in the approval process, some for several years despite similarity of product, and many others have announced an intent.

At the 2014 meeting of the Commercial Aviation Alternate Fuels Initiative (CAAFI), frustration was exhibited by many of the prospective producers who complained about the time and cost of the approval process. The following statements to that effect were included in the meeting summary by Mark Rumizen at the 2014 Coordinating Research Council (CRC) Aviation Meeting:

2

- "ASTM D4054 process too lengthy and costly"
- "Extensive fuel property and engine/aircraft testing"
- "Repeating same tests regardless of compositional similarities with previous fuel approvals"

The recommendation was that the industry should look for ways to safely reduce cost without sacrificing fuel quality and the effects on flight safety, air worthiness, durability, and maintenance.

2.2   Objective

The Objective of this report is to compare the results of compatibility tests of elastomeric materials exposed to synthesized hydrocarbon fuels and their blends with exposure to conventional Jet A/Jet A-1/JP-8 fuels. The purpose is to determine if exposure to hydrocarbon kerosenes containing synthesized hydrocarbons has the same effect on elastomers as exposure to conventional jet fuel.

2.3   Scope

The presentation and discussion will focus on data from two separate evaluations:

1. Results from the materials compatibility tests contained in the technical reports of evaluated synthesized fuels; these tests were conducted at elevated temperatures.
2. Results from tests to evaluate the effect of aromatics on volume swell of selected materials at ambient temperature

3.0 METHODS, ASSUMPTIONS, AND PROCEDURES

3.1 Materials Compatibility Evaluations of Synthesized Hydrocarbon Fuels and Blends

3.1.1 Materials

With the exception of the very early fuel evaluations, most of the fuels have been screened for materials compatibility using a reduced list of materials rather than the entire matrix of materials listed in Table A3.2 of ASTM D4054-15. This subset is termed the "short-short list" that the engine and airframe OEMs have agreed upon for the purposes of screening for potential compatibility issues. The materials of the short-short list are listed in Table 1 along with the property tests and soak conditions.

Table 1. Materials and Test Conditions

	Material and Test Conditions	Tests	
Coatings	28 days @ 200°F (93°C) (all) • BMS 10-20 (epoxy) • BMS 10-39 (epoxy) • MIL-P-24441 (epoxy polyamide)	• Pencil hardness • Tape adhesion	• ASTM D3363 • ASTM D3359/A
Sealants	28 days @ 200°F (93°C) (all) • PR 1828 B-2 (AMS 3277) (polythioether) • PR 1776 B-1/2 (AMS 3281) (polysulfide)	• Peel strength • Volume change • Hardness • Tensile strength	• SAE AS5127/1 • ASTM D471 • ASTM D2240 • ASTM D412
O-rings	28 days at indicated temperature • Nitrile (N602-70): @ 260°F (127°C) • Fluorosilicone (L1120-70): @ 225°F (107°C) • Viton GLT (VO835-75): @ 325°F (163°C)	• Tensile strength • Volume change • Hardness/Shr M • Compression set	• ASTM D1414 • ASTM D471 • ASTM D2240 • ASTM D395

3.1.2 Fuels

The synthesized fuels and blends reviewed in this section are those fuels which have undergone a formal review process by the aviation fuel community and for which formal reports are available. Reported data were found for a total of 16 synthesized hydrocarbon fuels and/or their blends with conventional jet fuels. These fuels are listed in Table 2 according to their category of synthesis.

- Fischer-Tropsch (F-T) processed fuels from synthesis gas including those with aromatics
- Hydroprocessed Ethers and Fatty Acids (HEFA)
- Other fuels from renewable sources, e.g., alcohol to jet (ATJ), Hydrotreated Depolymerized Cellulosic Jet (HDCJ), and Catalytic Hydrothermolysis (CH)

Table 2. Fuels and Materials Evaluated

Fuel	Property	Ref.	Coatings			Sealants		O-Rings		
			BMS 10-20	BMS 10-39	MIL-P-24441	PR-1828	PR-1776	N0602	L1120	V0835
F-T Fuels	Sasol IPK	[4]				X				
	Sasol IPK/Jet A-1	[4]				X				
	Syntroleum S-8	[4]	X	X	X	X	X	X	X	X
	Syntroleum. S-8/JP-8	[4]	X	X	X	X	X	X	X	X
	Shell GTL	[4]				X				
	Shell GTL/JP-8	[4]				X				
	Sasol FSJF	[5]	X	X	X	X	X	X	X	X
	Sasol IPK/A	[5]	X	X	X	X	X	X	X	X
	Sasol IPK/A / Jet A-1	[5]	X	X	X	X	X	X	X	X
HEFA	R-8	[4]	X	X	X	X	X	X	X	X
	R-8/JP-8	[4]	X	X	X	X	X	X	X	X
	UOP	[4]				X				
	UOP/JP-8	[4]				X				
	EERC	[4]				X				
	EERC/JP-8	[4]				X				
Other Renew-ables	Gevo ATJ	[6]	X	X	X	X	X	X	X	X
	Gevo/JP-8	[6]	X	X	X	X	X	X	X	X
	Amyris SIP/Jet A	[7]	X	X	X	X	X	X	X	X

3.1.3 Graphic Presentations

In the graphs summarizing the results of these evaluations, the aromatic content of the fuel is indicated and decreases from left to right; the exceptions to this model are the results on hardness for O-rings, which will be explained at the time of presentation. Also, the fuels are color-coded as follows:

- Black – unaged
- Blue – conventional jet fuel
- Violet – blend of synthesized fuel with conventional fuel
- Red – synthesized fuel
- Cross-hatched red or violet – fuel with synthesized aromatics

3.1.4 Coatings

Figures 1 and 2 present the results of compatibility tests on the three coatings listed in Table 1. The results for the three coatings are combined into single graphs since the results were the same.
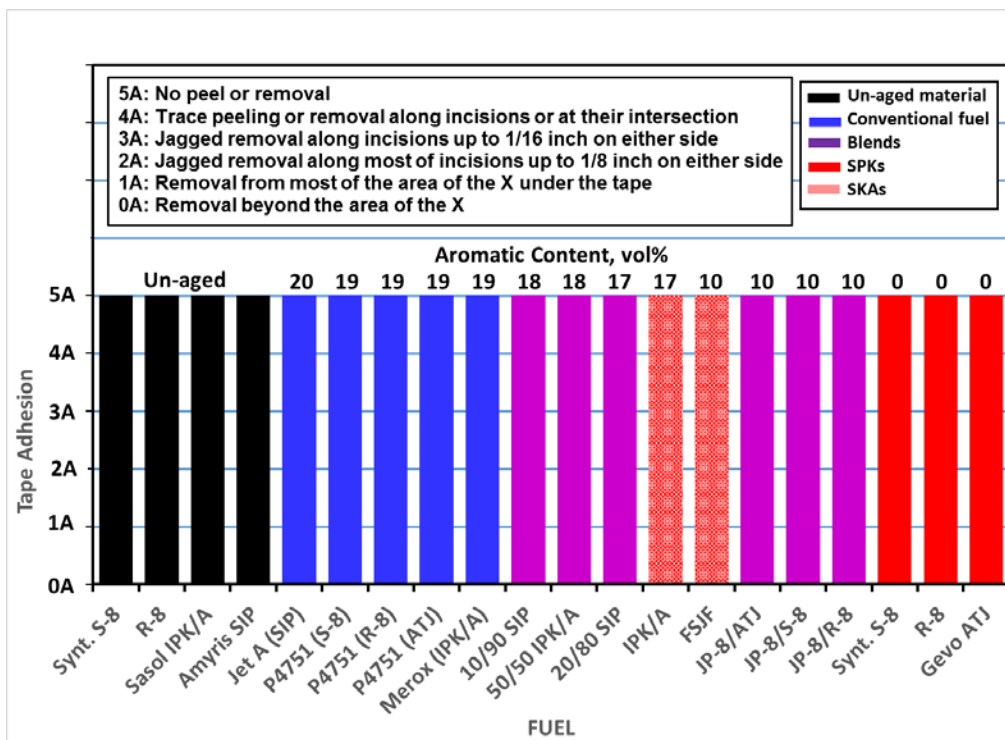
Figure 1. Fuel Effects on Tape Adhesion for BMS 10-20, BMS 10-39, and MIL-P-24441 Coatings Soaked in Test Fuel at 200°F (93°C) for 28 Days
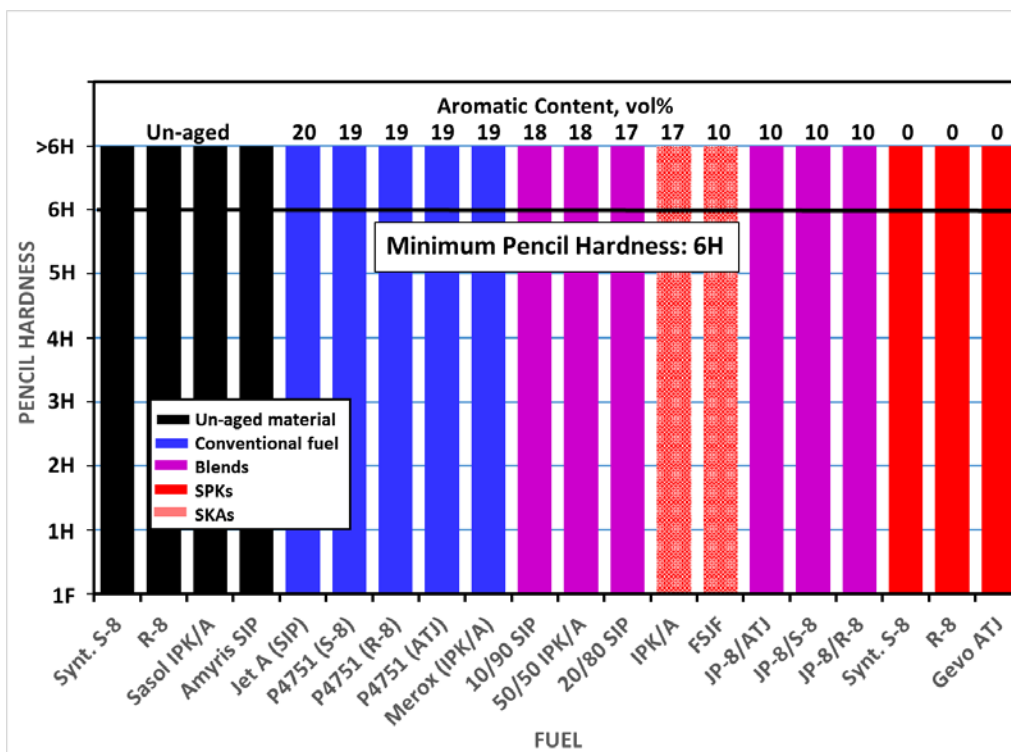

Figure 2. Fuel Effects on Pencil Hardness for BMS 10-20, BMS 10-39, and MIL-P-24441 Coatings Soaked in Test Fuel at 200°F (93°C) for 28 Days

The results of the coating evaluations are summarized below:

- Tape adhesion: There is no formal minimum requirement for adhesion; pass/fail criteria are considered to be up to the customer. The rating definitions are listed on the graph. All three materials exhibited "no peel or removal", the highest rating. Therefore, there were no fuel effects on the adhesion of these coatings.
- Pencil hardness: The Pencil Hardness Test is used by industry to test coatings for their hardness and resistance to scratches and wear. All three materials showed excellent resistance to scratch and wear by exceeding the minimum requirements of no scratch with a 6H pencil.

In summary, there were no differences in the results of the fuel compatibility tests on any of the three coatings regardless of the presence of aromatics, synthesized or natural.

3.1.5 Sealants

The results of compatibility tests on the two sealants listed in Table 1 are presented in Figures 3a to 3e for PR 1828 B-2 (polythioether)and Figures 4a to 4e for PR 1776 B-1/2 (polysulfide). Only twelve synthesized fuels and blends were evaluated on PR 1776, while nineteen were evaluated on PR 1828 with the addition of several more HEFA fuels and blends. The results will be discussed separately.

3.1.5.1 PR 1828 B-2 (AMS 3277) (Polythioether)

For this sealant, the effect of fuel on tensile strength seems quite random, and shows no correlation with aromatic content. However, all of the test results were well above the minimum technical requirements of 200 psi.

Elongation was substantially reduced for almost all of the fuels, with many being very near or slightly below the minimum of 150%. For the two that were below the minimum, the results with the base JP-8 were also slightly below the minimum; hence, this may have been a problem with the sealant sample itself rather than a fuel-related issue.

Volume swell shows a definite trend toward decreasing change with decreasing aromatic content. All changes are less the 8% allowable volume change for this material.

Exposure to fuel, regardless of source or aromatic content, always reduced the hardness of this sealant. There was no apparent correlation with aromatic content. All of the results were above the minimum hardness of 35 for this sealant compound.

As with the tensile strength, the results for fuel effects on peel strength were very random, even with the conventional JP-8s. All tests met the minimum requirement of 20 lbs.

In summary, all of the fuel evaluations with PR 1828 B-2 (polythioether) sealant met the technical requirements of the material with a couple minor exceptions which appear to have been a problem with the sealant compound since the results of the base fuel were unusual compared to the other base fuels.
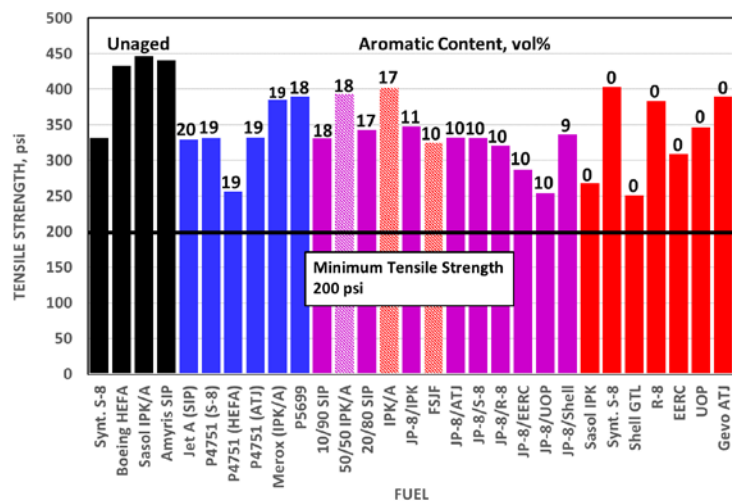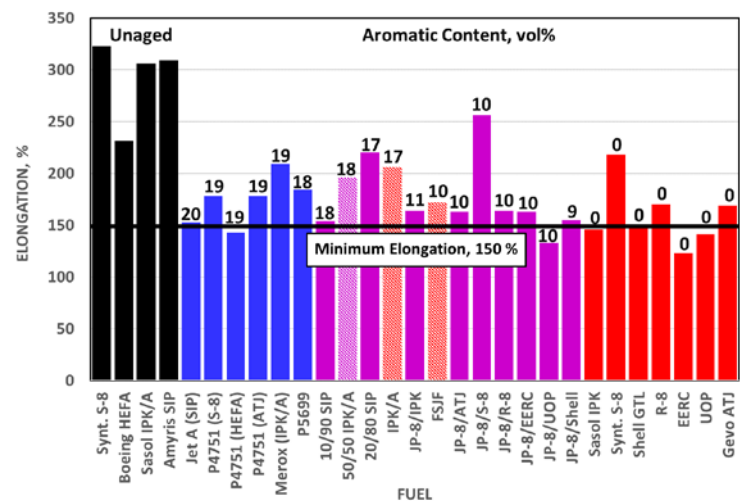
Figure 3a. Tensile strength
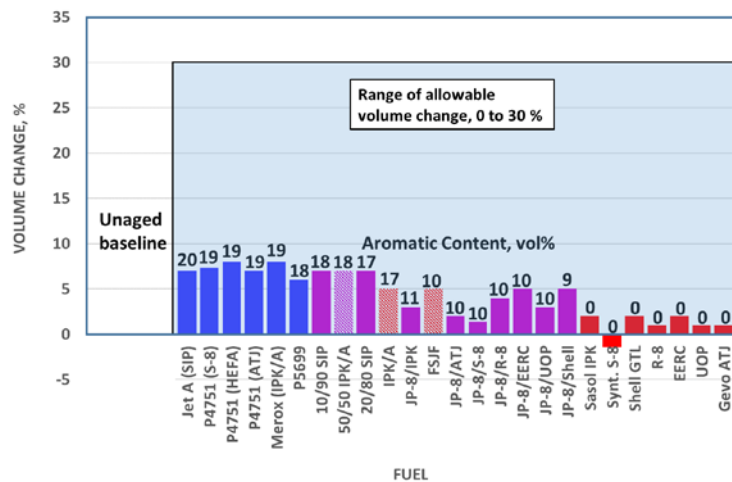

Figure 3b. Elongation
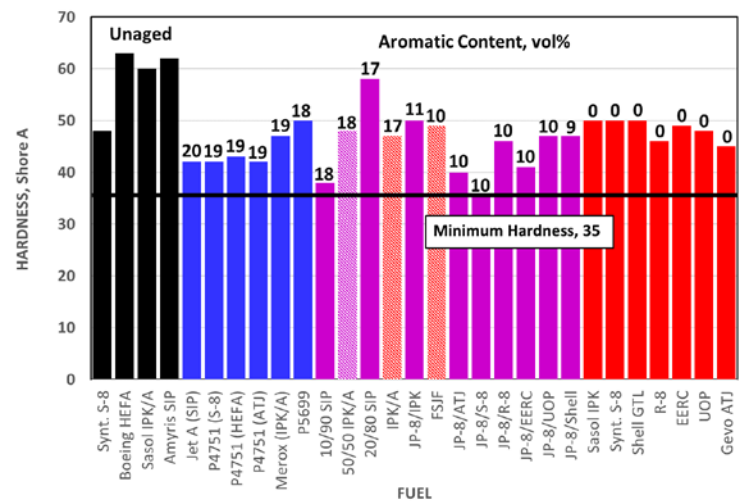

Figure 3c. Volume Change

Figure 3d. Hardness

Figure 3. Fuel Effects on PR 1828 B-2 Sealants Soaked in Test Fuel at 200°F (93°C) for 28 Days
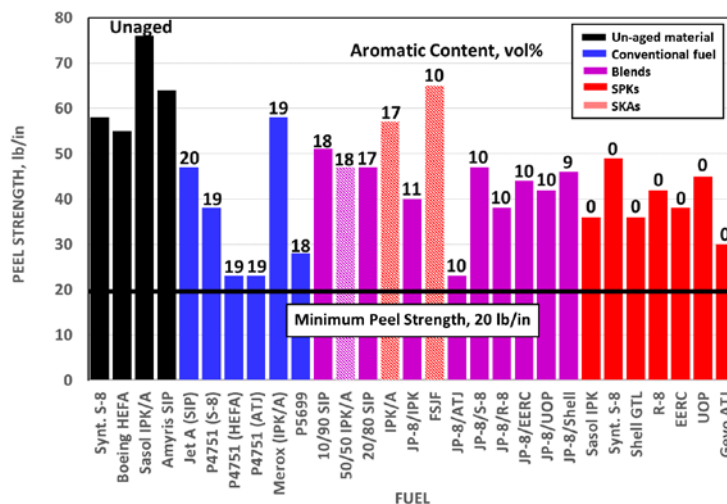
Figure 3e. Peel Strength

**Figure 3. Fuel Effects on PR 1828 B-2 Sealants Soaked in Test
Fuel at 200°F (93°C) for 28 Days** *(Cont'd)*

3.1.5.2 PR 1776 B-2 (AMS 3281) (Polysulfide)

For this sealant, the effect of fuel on tensile strength showed a reduction in tensile strength with the conventional fuels and blends, but little effect with the blends and zero-aromatic fuels. However, all of the test results were above the minimum technical requirements of 200 psi (1.39 kPa).

As with the other sealant, elongation was substantially reduced with all of the fuels, with several being very near or slightly below the minimum of 150%. For the SIP fuel and blend that were slightly below the minimum, the results with the base JP-8 was much lower than for the other base fuels; hence, this may have been a problem with the sealant sample itself rather than a fuel-related issue.

The results of the tests on volume swell were very different than with the previous sealant. All fuel tests, except for the Sasol conventional and synthetic fuels, resulted in shrinkage, including the tests with conventional fuels. All changes are less the 30% allowable volume change for this material.

With this sealant, exposure to fuel always resulted in hardness that met the minimum requirement of 35. There appeared to be a slight increase in hardness with decreasing aromatic content.

Exposure to fuel had less effect on peel strength for this sealant than for the previous sealant; exposure to all fuels met the minimum requirement of 20 lbs.

In summary, all of the fuel evaluations with PR 1776 B-1/2 (polysulfide) sealant met the technical requirements of the material with a couple minor exceptions which appear to have been a problem with the sealant sample since the results of the base fuel were unusual compared to the other base fuels.
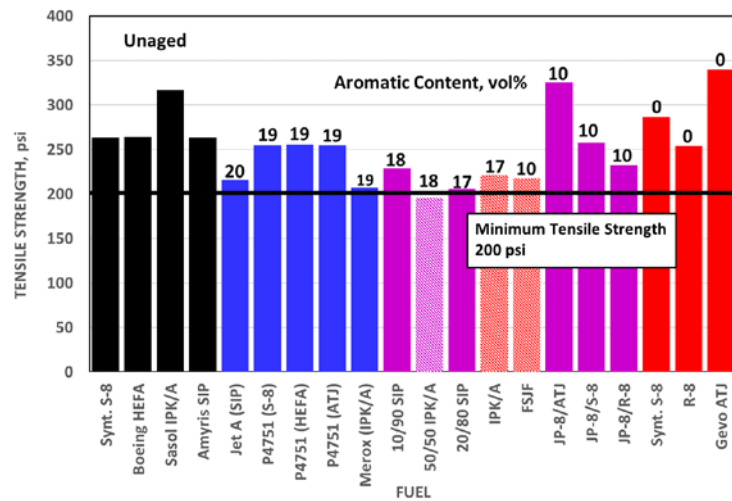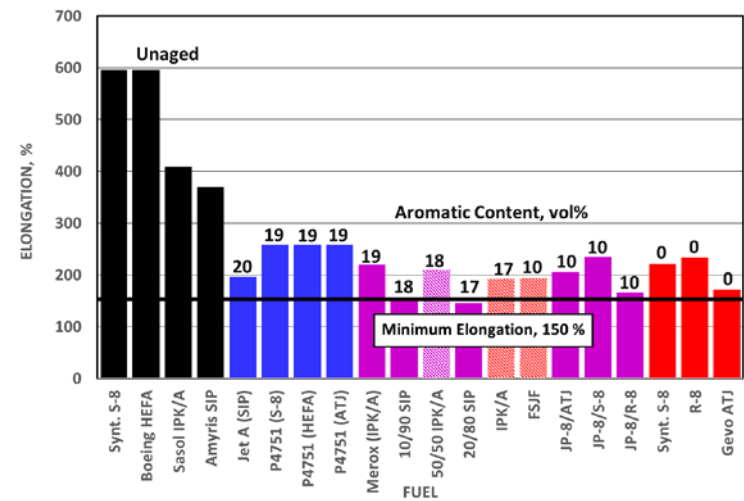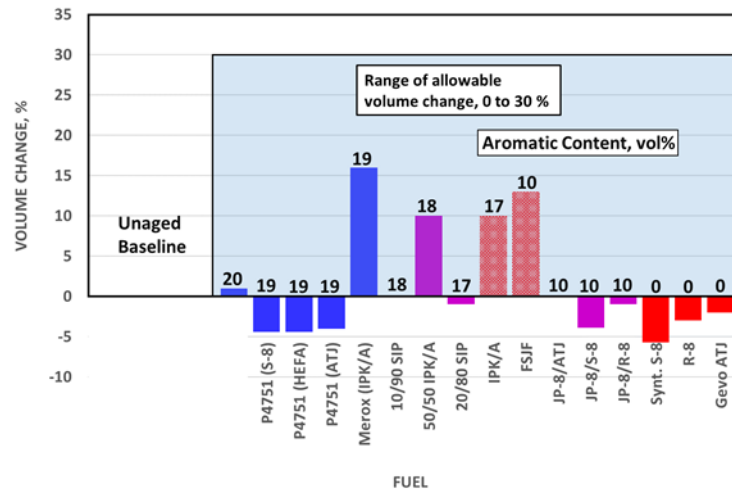
9

Figure 4a. Tensile Strength
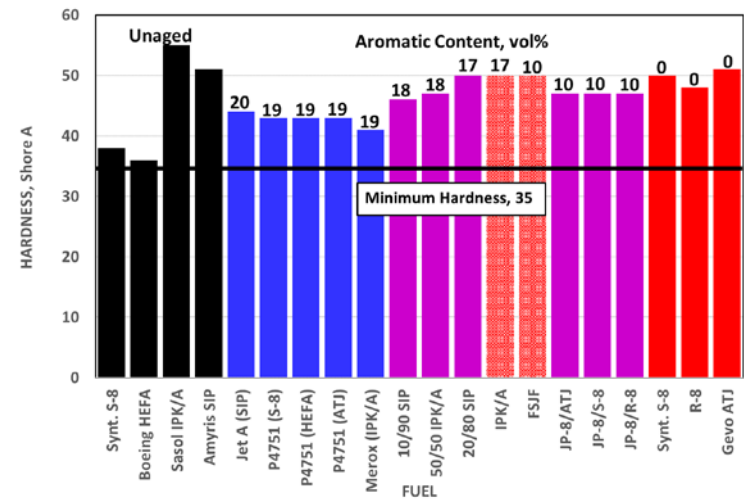

Figure 4b. Elongation

Figure 4c. Volume Change

Figure 4d. Hardness

Figure 4. Fuel Effects on PR 1776 B-1/2 Sealants Soaked in Test Fuel at 200°F (93°C) for 28 Days
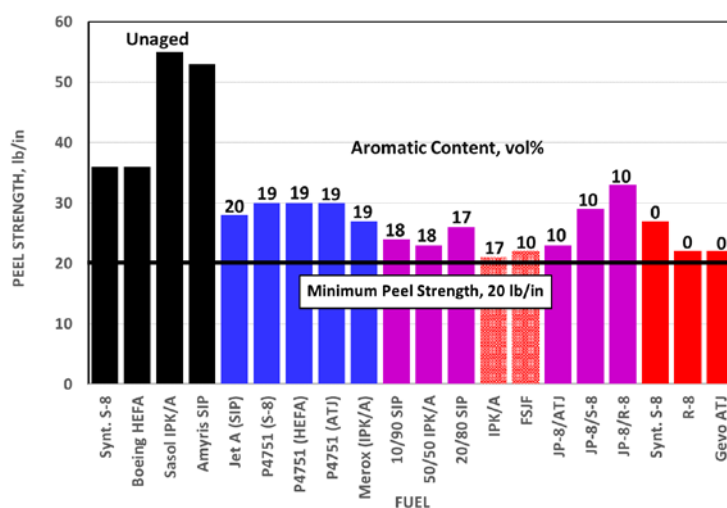
Figure 4e. Peel Strength

**Figure 4. Fuel Effects on PR 1776 B-1/2 Sealants Soaked in Test
Fuel at 200°F (93°C) for 28 Days** *(Cont'd)*

3.1.5.3 Summary of Fuel Exposure on Sealants

Although exposure to fuels did result in changes in the performance properties, there were no significant differences between the results with conventional fuels and with the synthesized fuels. The presence of synthesized aromatics, created by different methods in the Sasol fuels, showed no concerns; the results of exposure to these fuels was the same as with conventional fuels of similar aromatic content.

3.1.6 O-Rings

The results of compatibility tests on the three O-ring materials listed in Table 1 are presented in Figures 5a to 5e for N0602 (nitrile), Figures 6a to 6e for L1011 (fluorosilicone), and Figures 7a to 7e for VO-835 (fluorocarbon). Eleven synthesized fuels and blends were evaluated on all three O-ring materials. The results will be discussed separately.

3.1.6.1 N0602 (AMS-P-5315) (Nitrile)

For this O-ring material, the effect of fuel on tensile strength seems quite random, and shows no correlation with aromatic content. Some fuels resulted in a moderate decrease of tensile strength, while others were minimal. However, all of the test results were well above the minimum technical requirements of 1,000 psi.

Elongation was reduced with all of the fuels, with several being very near the minimum of 200%. The difference among the fuels was only about ±10%. This property should not be of too much concern as it relates to stretch required to install O-rings.

Figure 5a. Tensile Strength

Figure 5b. Elongation
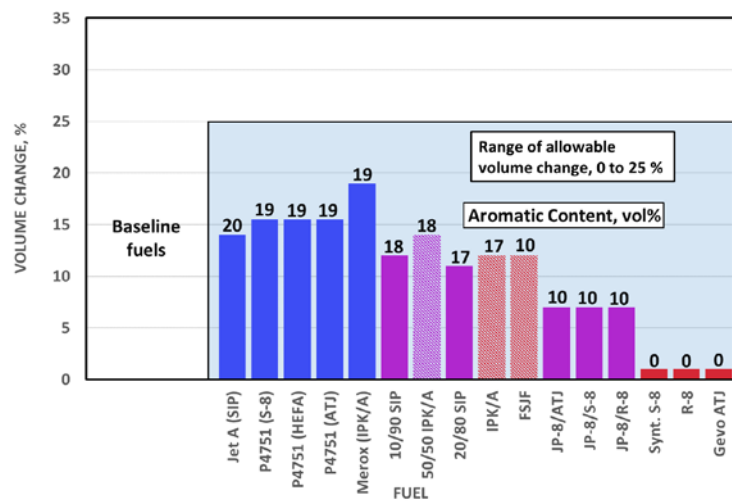
Figure 5c. Volume Change
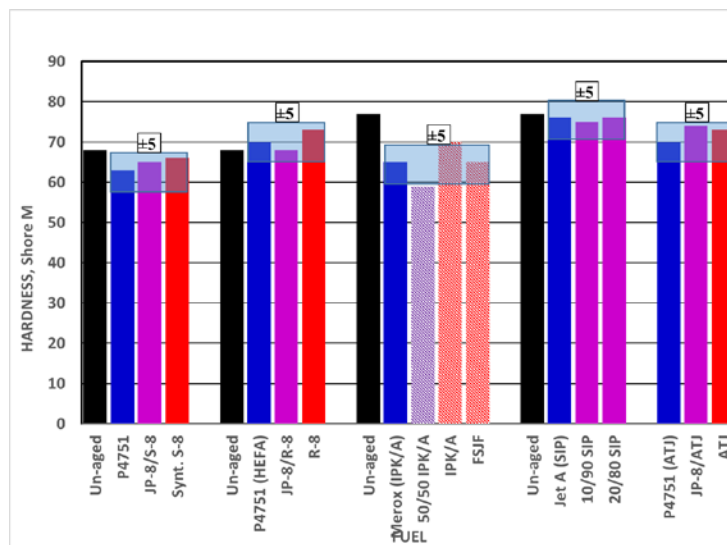
Figure 5d. Hardness

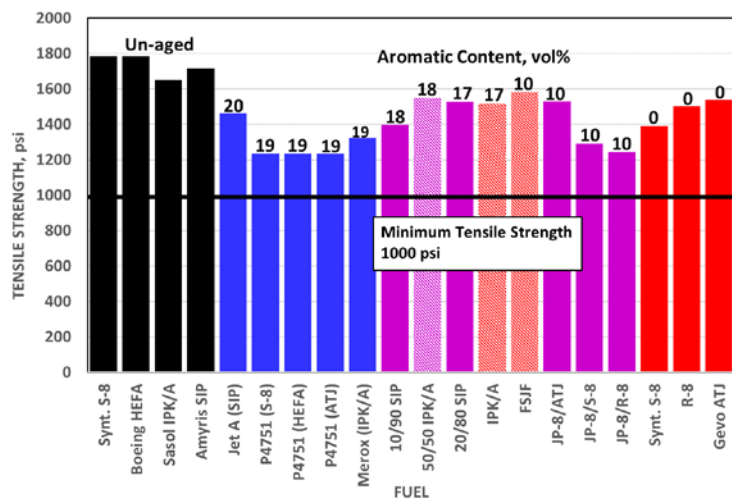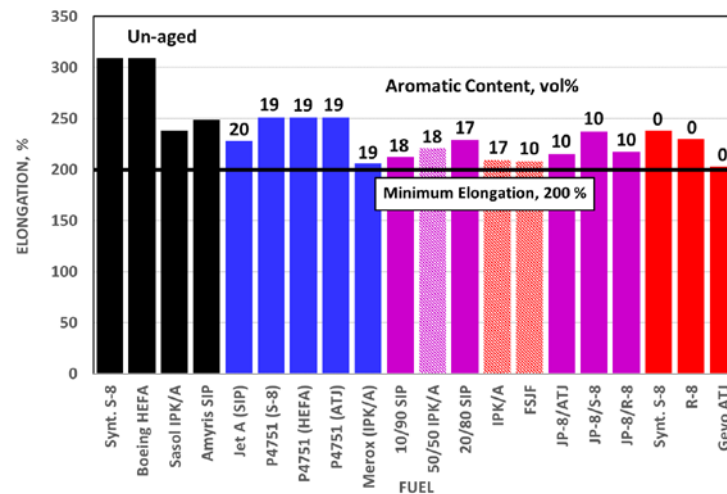**Figure 5. Fuel Effects on N602 (AMS-P-5315) Nitrile O-Rings Soaked in Test Fuel at 260°F (127°C) for 28 Days**
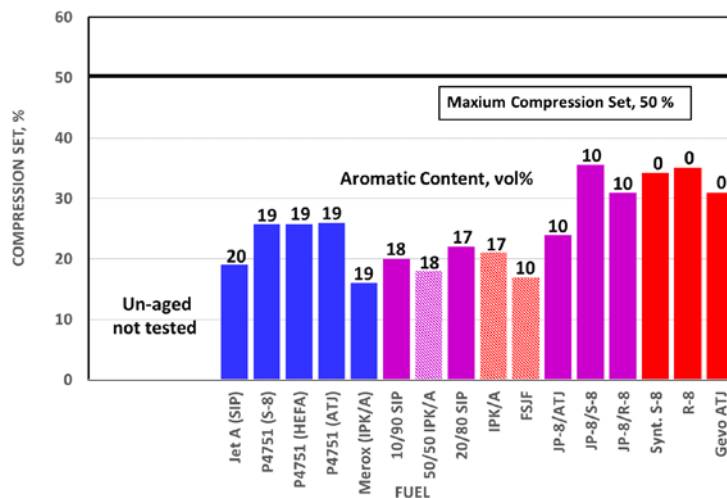
Figure 5e. Compression Set

Figure 5. Fuel Effects on N602 (AMS-P-5315) Nitrile O-Rings Soaked in Test Fuel at 260°F (127°C) for 28 Days *(Cont'd)*

Volume swell shows a definite trend toward decreasing change with decreasing aromatic content regardless of fuel source; this will be further supported in Section 4.1 Effect of Aromatics on Volume Swell. All changes are less the 25% allowable volume change for this material.

The acceptance criteria for hardness is different than the other properties in that it is relative to the base fuel rather than absolute limit. For this reason, the results are grouped by fuel rather than aromatic content. There was very little change in the hardness of this material caused by fuel exposure. The variation in each set is within ±5% which is the accuracy of the test method. It might be better if there was an absolute technical requirement.

Compression set generally increased with aromatic content, but all were significantly lower than the maximum technical limit of 50%.

3.1.6.2 L1120 (AMS-R-25988) (Fluorosilicone)

Although the fluorosilicone material showed some sensitivities to fuel exposure in general, as well as to aromatics specifically, the effect was less than that of the previous nitrile material.

The tensile strength generally increased with decreasing aromatic content, but in each case was above the required technical minimum.

The only fuels that resulted in an elongation that was near the limit were conventional fuels. Evaluations with the blends and pure synthesized fuels all showed better elongation limits.

Figure 6a. Tensile Strength
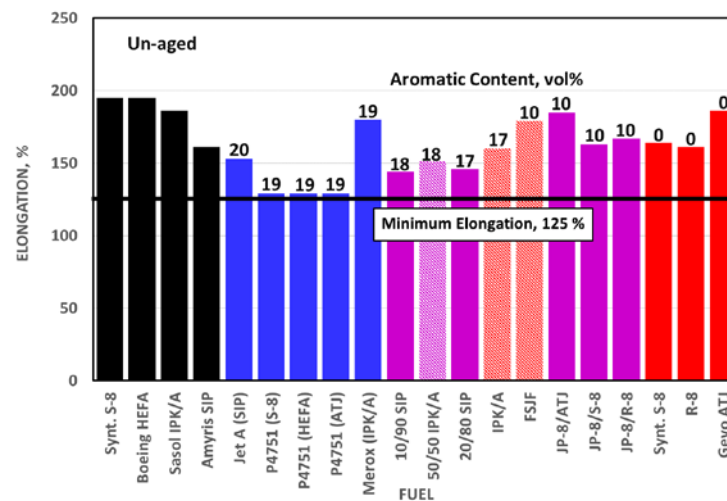

Figure 6b. Elongation
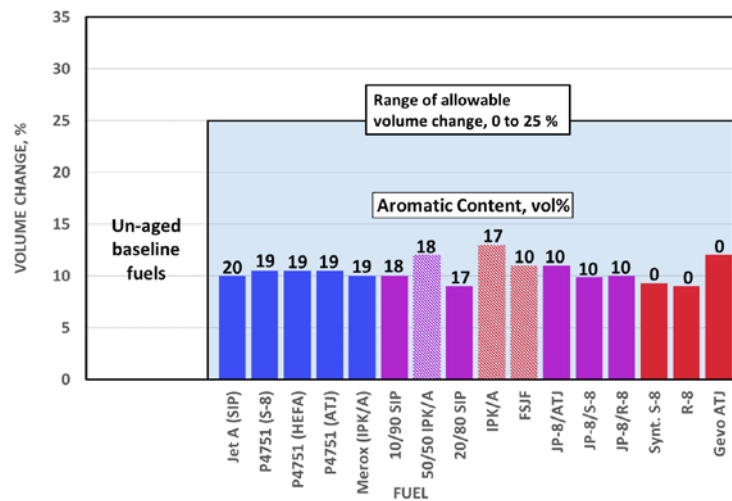
Figure 6c. Volume Change
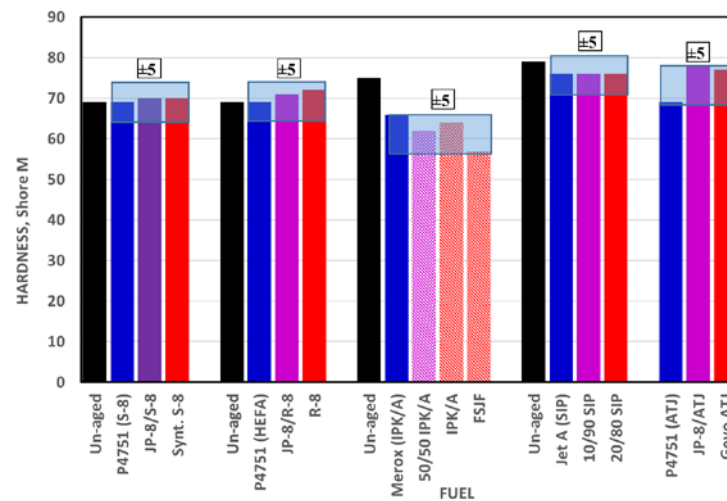
Figure 6d. Hardness

Figure 6. Fuel Effects on L1120 (AMS-R-25988) Fluorosilicone O-Rings Soaked in Test Fuel at 225°F (107°C) for 28 Days
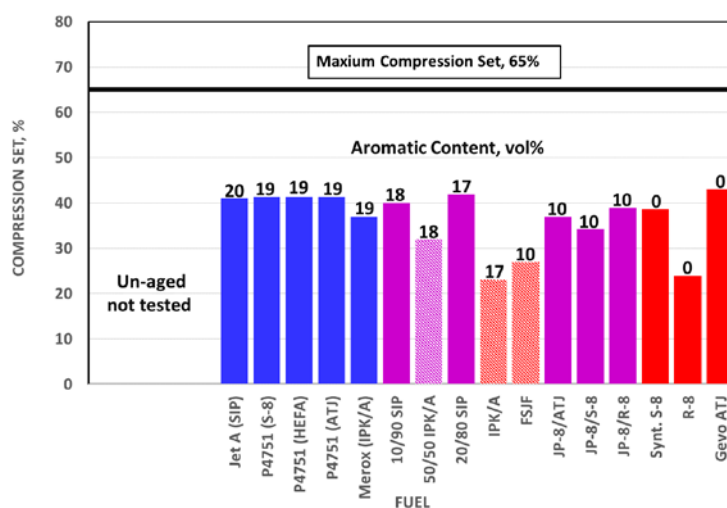
Figure 6e. Compression Set

Figure 6. Fuel Effects on L1120 (AMS-R-25988) Fluorosilicone O-Rings Soaked in Test Fuel at 225°F (107°C) for 28 Days *(Cont'd)*

There was very little difference in the volume change among the fuel evaluations; aromatic content had very little effect. All results were well within the acceptable range of 0 to 25%. Similarly, there was very little change in hardness, and all samples fell with ±5%, the accuracy of the test method.

There was no trend of aromatics on compression set with the fluorosilicone O-rings; all results were significantly less than the technical limit of 65%.

3.1.6.3 V0835 Viton GLT (Fluorocarbon)

In general, Viton (fluorocarbon) materials are considered relatively unaffected by fuel exposure including variation in aromatic content. This was realized in these evaluations.

There was very little difference among the fuels on tensile strength with the exception of the tests with the Sasol fuels. However, the tensile strength of the unaged material and the tests with conventional fuel were also high, so it is considered that this is due to the material samples and not due to the presence of synthesized aromatics.

There was very little difference in the elongation limit with the exception of the 10% blend of Amyris SIP; however, the result was not consistent with the 0%, 20%, and 100% SIP, so it is assumed the result is an aberration and not due to the presence of SIP.

The technical limit for volume change is only 8% compared to 25% for nitrile and fluorosilicone O-rings. However, all results were less than 8%, and any effect of aromatics was quite small.

As with the other O-ring materials, the fuel effects on hardness were acceptable, and there was no apparent effect of aromatics.
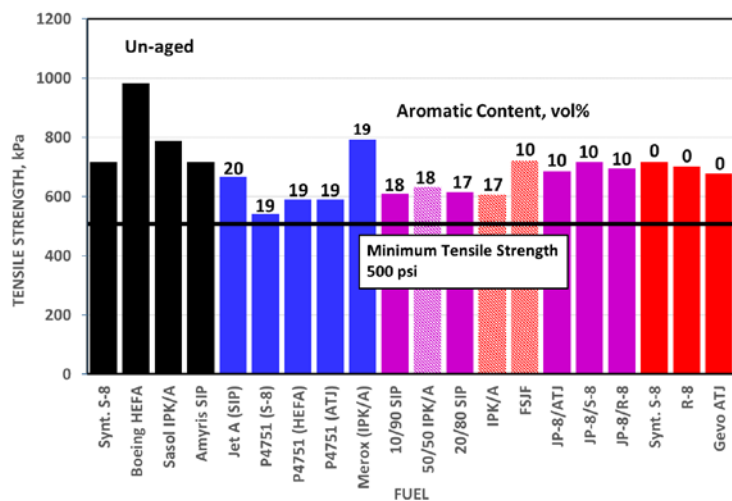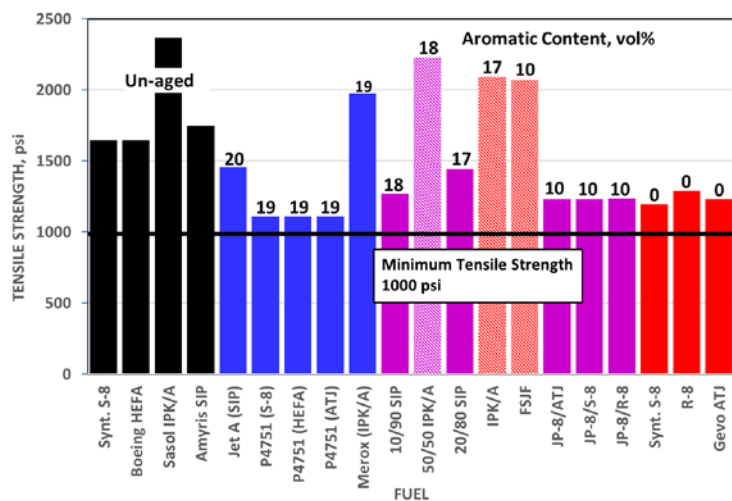
Figure 7a. Tensile Strength
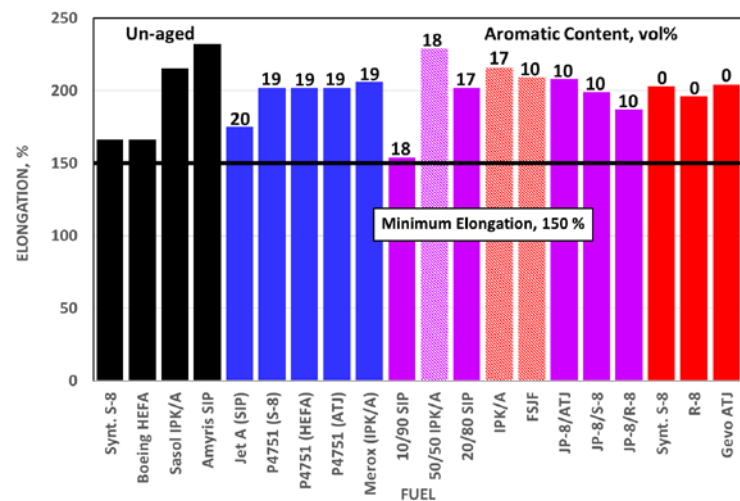

Figure 7b. Elongation
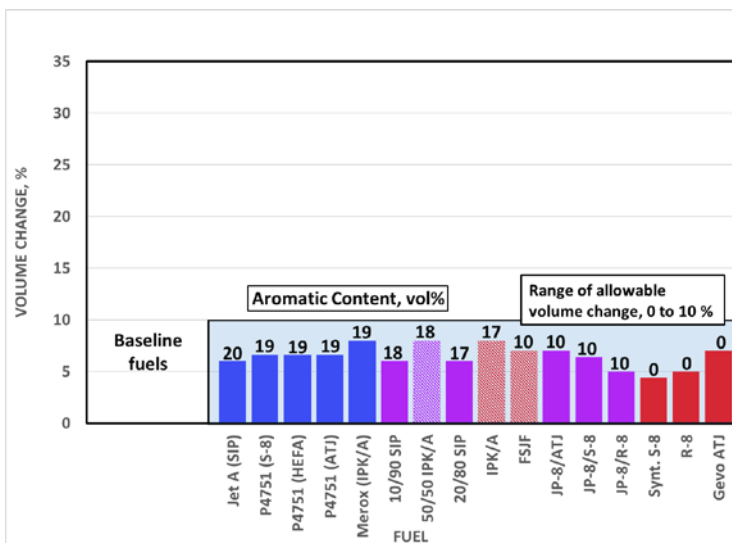
Figure 7c. Volume Change
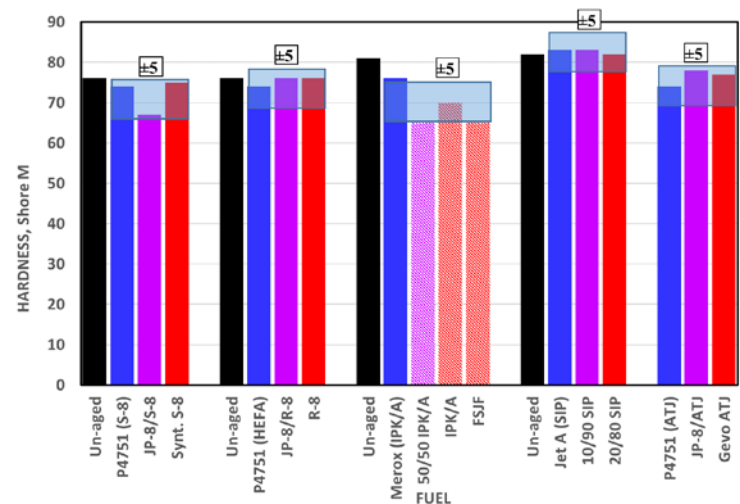
Figure 7d. Hardness

Figure 7. Fuel Effects on V0835 Viton GLT (Fluorocarbon) O-Rings Soaked in Test Fuel at 325°F (163°C) for 28 Days
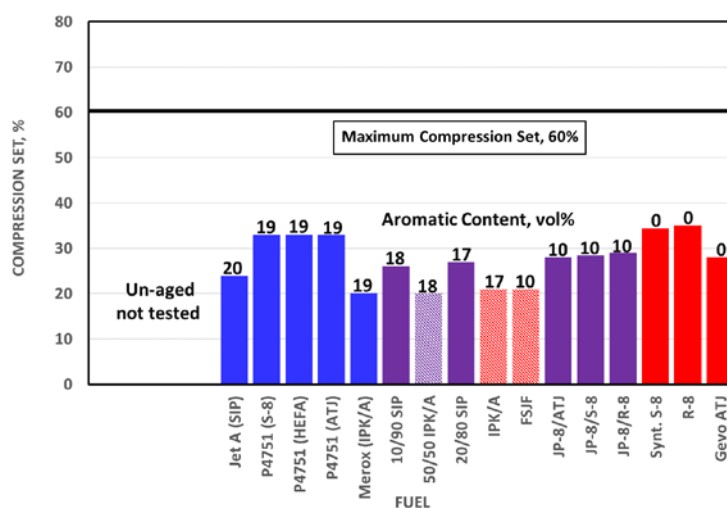
Figure 7e. Compression Set

Figure 7. Fuel Effects on V0835 Viton GLT (Fluorocarbon) O-Rings Soaked in Test Fuel at 325°F (163°C) for 28 Days *(Cont'd)*

Similar to the results with the nitrile O-rings, compression set with the Viton O-rings increased as the aromatic content decreased. However, in every case, the amount of compression set was significantly less than the technical limit of 60%.

3.1.6.4   Summary of Fuel Exposure on O-Rings

The results of all of the fuel tests on O-rings met the technical requirements of the individual materials. The results of exposure to fuels containing synthesized hydrocarbons was the same as with conventional fuels of similar aromatic content. The results with the Sasol fuels that contained synthesized aromatics, created by different two different methods, were the same as that for their reference fuels.

3.1.7   Summary of Materials Compatibility Tests

The properties of the coatings were unaffected by exposure to any of the test fuels.

With a few minor exceptions, the results of all of the fuel tests on sealants met the technical requirements. The few exceptions were considered due to the material sample. The results with the fuels containing synthesized hydrocarbons were in the same range as their conventional reference fuels of similar aromatic content.

The results of all of the property tests on the three O-ring materials met all of the technical requirements for that material property. The materials performed the same when exposed to fuels containing synthesized hydrocarbons as they did with conventional fuels of similar aromatic content.

The presence of synthesized aromatics, created by different methods in the Sasol fuels, showed no concerns; the results of exposure to these fuels were the same as with their conventional reference fuel.

4.0 RESULTS AND DISCUSSION

4.1 Effect of Aromatics on Volume Swell

4.1.1 Purpose and Scope

The purpose of the test results to be presented here is to demonstrate that elastomer materials which are sensitive to aromatics respond to aromatics in synthesized kerosenes the same as they do to aromatics in conventional jet fuels. Table 3 lists the 29 fuel-system elastomeric materials evaluated by Graham et al [8] for the sensitivity of volume swell to aromatic content. The 7 highlighted materials are those discussed in the previous section and will be the only materials presented here.

Table 3. Materials Evaluated for Sensitivity of Volume Swell to Aromatic Content

Category	ID	Material	Notes
O-rings	N0602	Nitrile Rubber	General Purpose
	L1120	Fluorosilicone	General Purpose
	V0747	Fluorocarbon	General Purpose
	V0835	Fluorocarbon	Low-temperature
	V1226	Fluorocarbon	Low-temperature
Fuel Barrier Materials	AC-603-01	Acrylic Nitrile	Hose, Aerial
	EC-614-01	Epichlorohydrin	Hose, Ground
	EF-51956	Nitrile Rubber	Bladder
	EF-5904C	Polyurethane	Bladder
Sealants	PR-1422	Polysulfide	Dichromate cured
	PR-1440	Polysulfide	Manganese dioxide cured
	PR-1776	Polysulfide	Manganese dioxide cured
	PR-1828	Polythioether	Epoxy cured
	PR-2911	Polythioether/Polyurethane	
	Q4-2817	Fluorosilicone	
Coatings	EC-776	Nitrile	
	C-27725	Polyurethane	
	BMS 10-20	Epoxy	
	BMS 10-39	Epoxy	
Adhesives	AF-10	Phenol-formaldehyde/ nitrile	
	Epon 828	Epoxy	
	FM-47	Vinyl Phenolic	
Composites	AS4-3501-6	Graphite/Epoxy	Low polymer loading
	IM7-5250-4	Graphite/Bismaleimide	Low polymer loading
Films	PE	Polyethylene	Non-polar
	PTFE	PTFE	
	Upilex	Kapton	
	Zytel	Nylon	
Foam	Foamex	Polyurethane	Open-celled foam

In this study by Graham et al, aromatic content was varied by using 9 different JP-8 fuels with aromatic contents ranging from 13.6 vol% to 23.6 vol% and blending them with various concentrations of Syntroleum S-8, an F-T kerosene meeting JP-8 property requirements but with zero aromatics. In all, there were 47 test fuels. Figure 8 summarizes the sensitivity of the different materials showing that nitrile materials, i.e., O-rings, bladder, and hose are the most sensitive; as a group, sealants were the next most sensitive. The coatings showed little or no sensitivity, which is consistent with the results presented earlier in Figures 1 and 2.
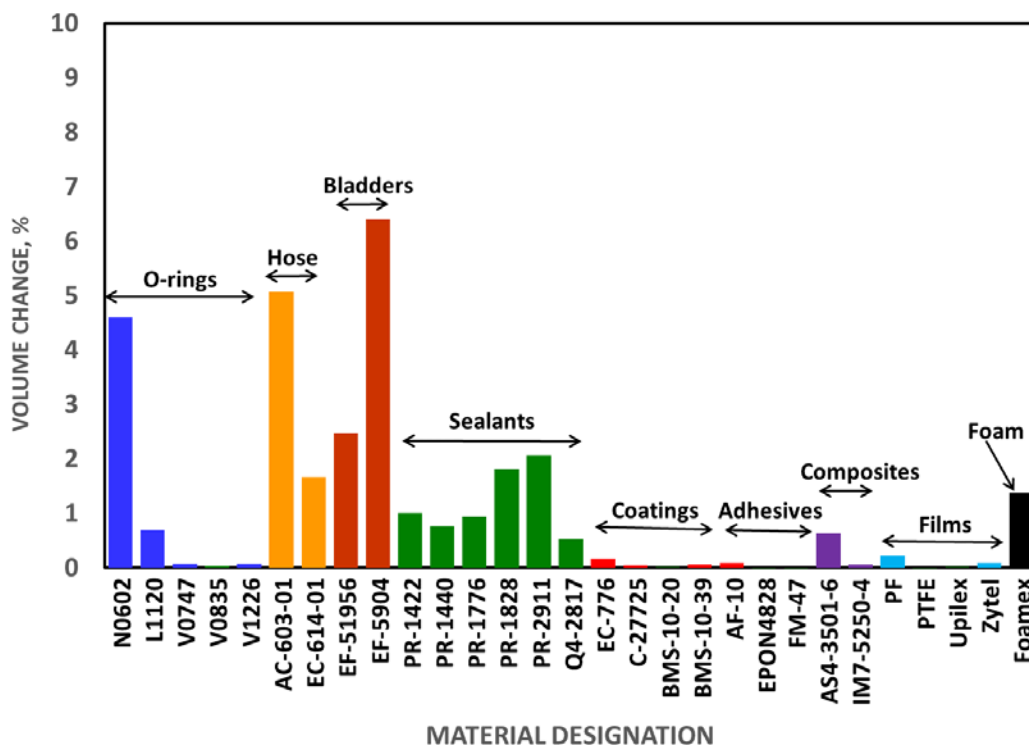
Figure 8. Comparative Sensitivity of Volume Swell to Aromatic Content for Fuel System Elastomers [8]

4.1.2   Evaluation of O-Rings for Sensitivity to Aromatic Content

The volume swell for O-rings was measured by optical dilatometry. [11] Figures 9, 10, and 11 show the effect of aromatics on volume swell for nitrile, fluorosilicone, and fluorocarbon O-rings from the list in Table 1 and highlighted in Table 3. The hollow and solid blue diamonds are the original data of Graham et al for the conventional JP-8s and blends with S-8, respectively. Data for several renewable kerosenes and their blends have been added to the original data. These fuels are identified Table 4; note that the aromatics in the ARA and KiOR products are synthesized aromatics. In each of these figures, the solid line is the mean of the data for the conventional fuels and blends. The dashed lines provide the 90% prediction intervals. Volume increases linearly with aromatic content for all three O-ring materials. The N0602 nitrile material has the strongest sensitivity, while the V0835 fluorocarbon is practically insensitive to aromatic content. N0602 is almost 7 times as sensitive to aromatic content as L1120 and 129 times as sensitive as V0835.
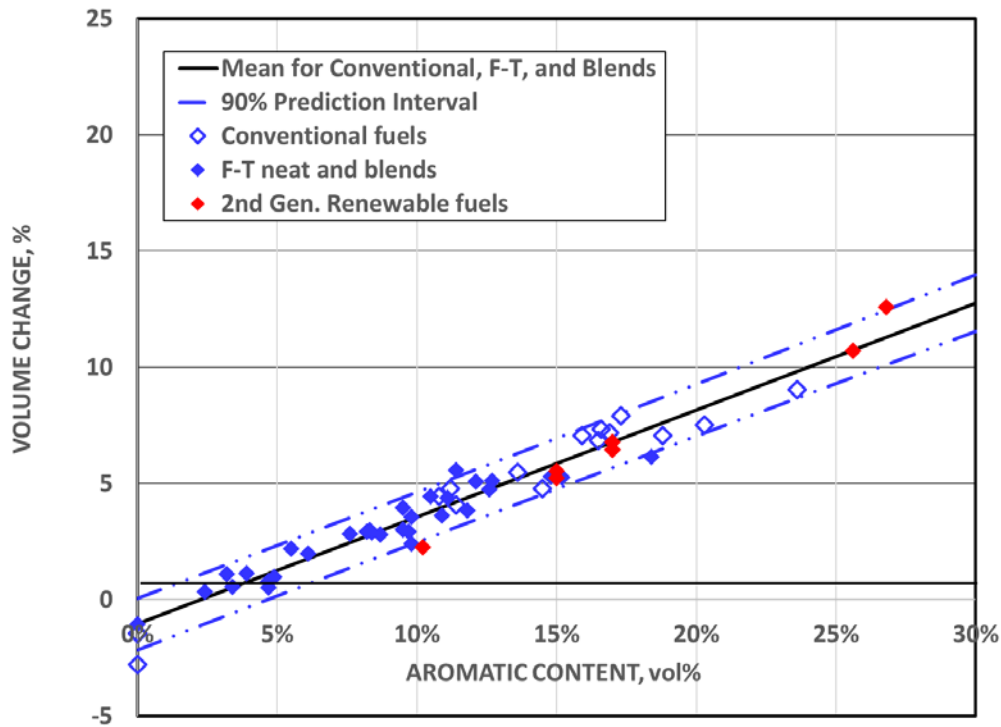
Figure 9. Effect of Aromatics on Volume Swell of N0602 Nitrile O-Rings at Ambient Temperature [6-10]
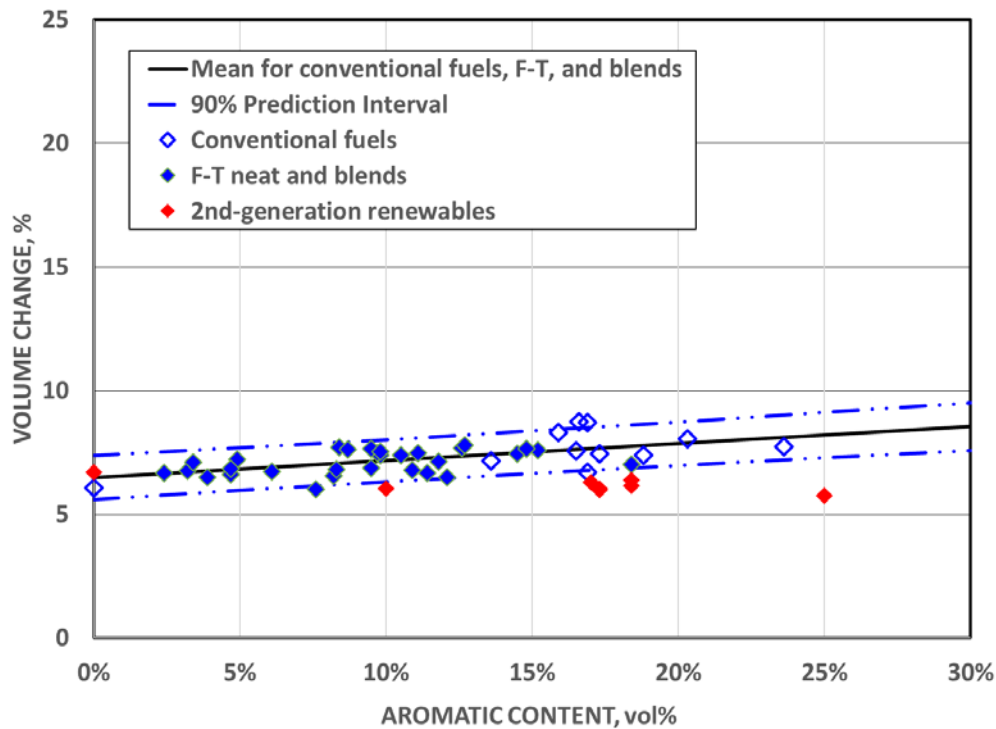
Figure 10. Effect of Aromatics on Volume Swell of L1120 Fluorosilicone O-Rings at Ambient Temperature [6-10]
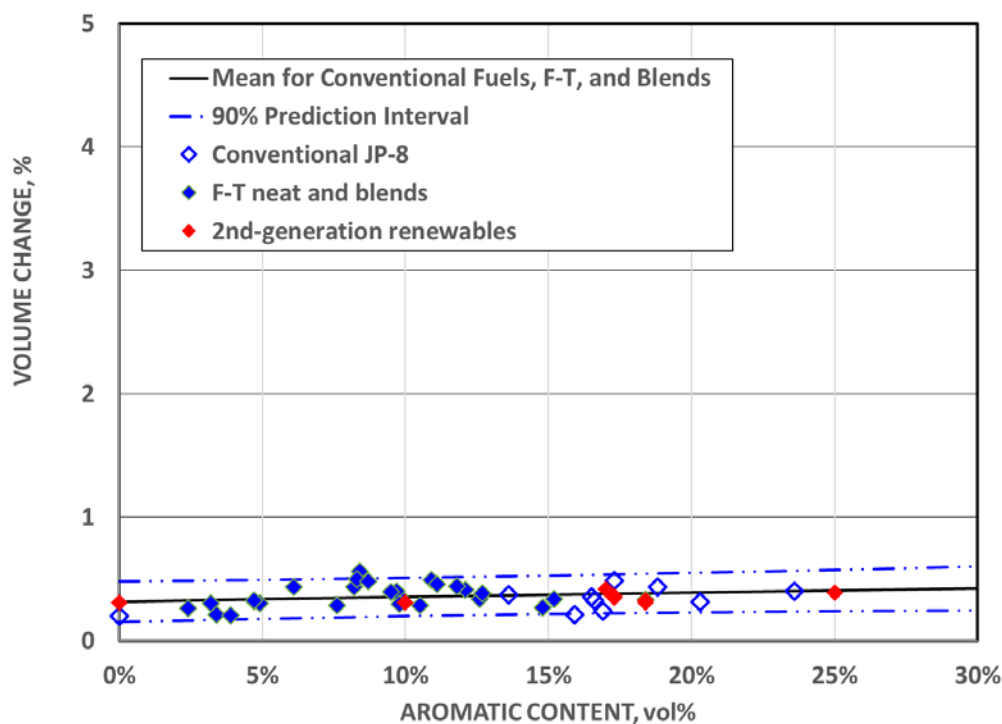
Figure 11. Effect of Aromatics on Volume Swell of V0835 Fluorocarbon O-Rings at Ambient Temperature [6-10]

Table 4. Renewable Fuels Added to Data for Figures 9 to 11

Fuel	Reference	Aromatic Content, vol%
ARA 100% ReadiJet	[9]	17.0
Amyris 10% SIP/JP-8 (POSF-9968)	[7]	18.4
Amyris 10% SIP/JP-8 (POSF-9970)	[7]	18.4
Amyris 20% SIP/JP-8 (POSF-9969)	[7]	17.3
Amyris 20% SIP/JP-8 (POSF-9971)	[7]	17.3
Gevo 100% ATJ	[6]	0
Gevo 50% ATJ/JP-8	[6]	10
KiOR 30% HDCJ/JP-8	[10]	25

These three figures show that the sensitivity of volume swell to aromatics is linear for these O-ring materials with very little scatter. Moreover, the sensitivities for the fuels containing synthesized aromatics fit the predictive model, except for the fluorosilicone material for which the sensitivities of all of the renewable fuels is a little lower than the predictive interval.

4.1.3 Evaluation of Sealant for Sensitivity to Aromatic Content

Figures 12 and 13 show the effect of aromatics on volume swell of the 2 sealants in Table 3. Similarly, Figures 14 and 15 show the effect of aromatics on 2 of the 3 coatings. There are no

data for these materials for the renewable fuels. The sensitivities of volume swell are linear with aromatic content with very little scatter, although for the coatings, the sensitivity is essentially zero.
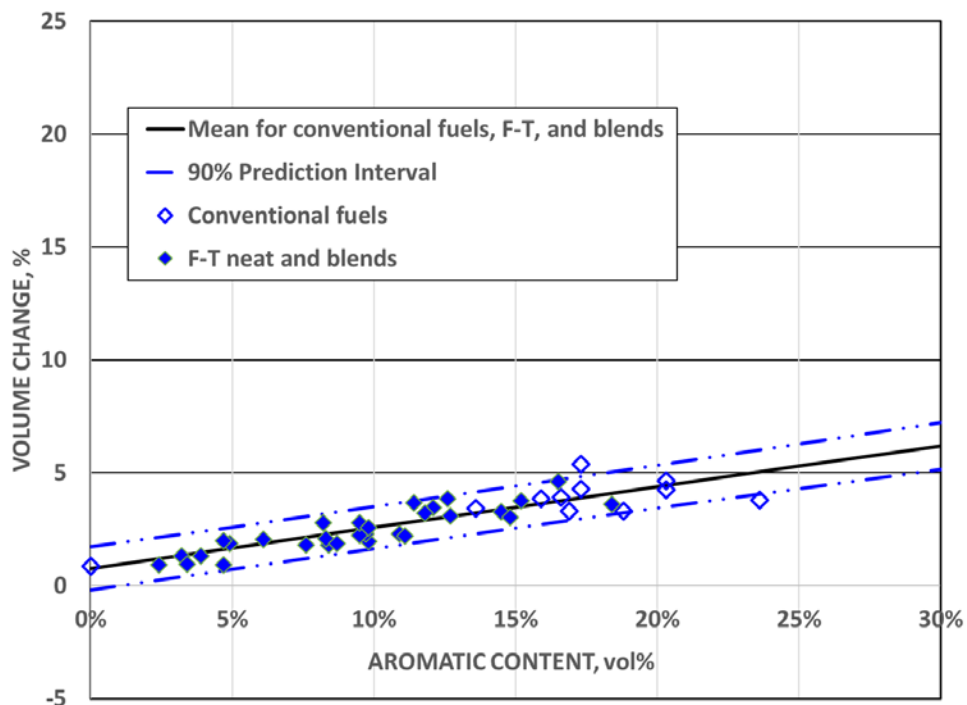
Figure 12. Effect of Aromatics on Volume Change of PR-1828 Sealant (Polythioether) [6]
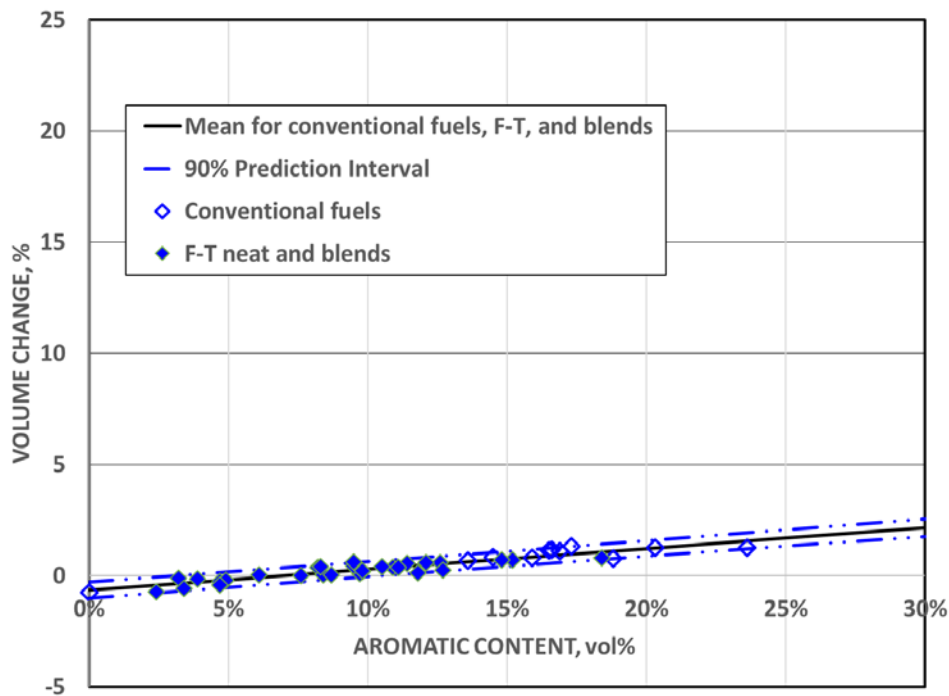
Figure 13. Effect of Aromatics on Volume Change of PR-1776 Sealant (Polysulfide) [6]
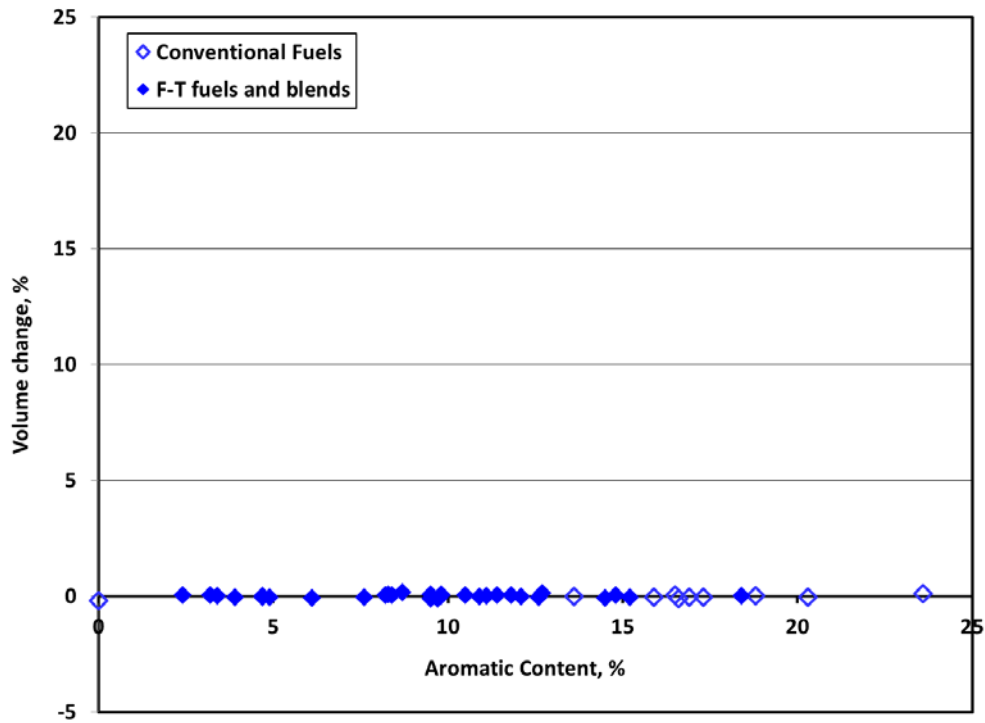
Figure 14. Effect of Aromatics on Volume Change of BMS 10-20 Coating (Epoxy) [6]
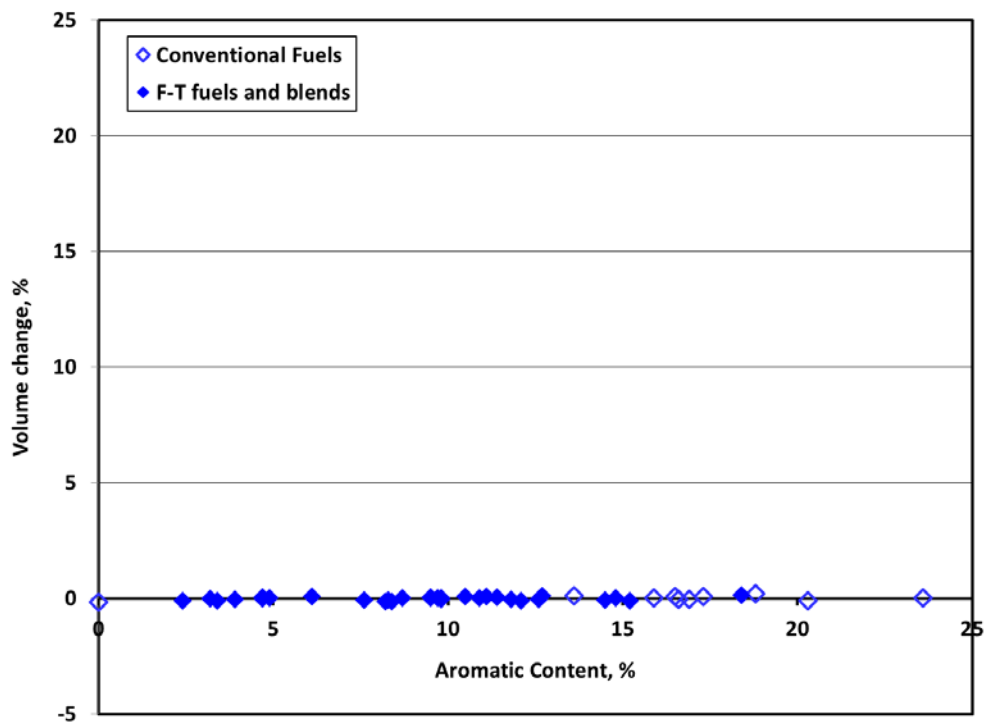
Figure 15. Effect of Aromatics on Volume Change of BMS 10-39 Coating (Epoxy) [6]

4.1.4 Discussion of Effect of Aromatics on Volume Swell

It is obvious that for the materials presented in Figures 9 through 15 that, when careful measurements are conducted, the effect of aromatics on volume swell of O-rings and sealants is linear; in addition, there is no apparent effects of fuels on volume swell for these coatings.

The 3 O-ring materials were the only materials for which there were equivalent data from the same laboratory on renewable fuels. Two of the renewable fuels contained synthesized aromatics and significant levels of cyclo-paraffins. The data for these two fuels fit the predictive model generated for conventional fuels and their blends with F-T fuels.

Although not presented here, the data for the other materials identified in Table 3 showed similar results. Where there was a sensitivity to aromatics, as shown in Figure 8, the effect was linear with very little scatter; the scatter was essentially zero for those materials that showed no effect as presented in Figure 8. The one exception was the series of tests on the Foamex polyurethane foam for which there was a lot scatter in the data regardless of aromatic content.

It is worthwhile at this point to consider the types of aromatics that were in the base fuels in this study of volume swell by Graham et al to determine if a simple control of aromatic content is sufficient or if further knowledge is necessary, e.g., tetralins and indans. Table 5 presents a summary of the GCxGC hydrocarbon analyses performed at UDRI for the base fuels. [12]

Table 5. Hydrocarbon Composition (GCxGC) of JP-8 Base Fuels for Figures 9 – 14 [9, 10, 12]

Hydrocarbon Family	POSF Number									
	3166	3602	3694	3773	4177	4751	4908	4911	ARA[1]	KiOR[2]
n-paraffins	22.4	16.0	19.6	19.7	12.6	18.8	19.5	15.7	33.6	16.6
Iso-paraffins	27.0	19.3	24.5	32.0	26.1	31.7	26.1	31.8	8.8	22.0
Cyclo-paraffins	22.6	29.8	30.3	22.2	28.5	20.6	30.7	25.4	28.2	18.8
Dicyclo-paraffins	7.7	9.4	7.4	6.1	12.3	5.7	9.4	8.3	9.7	11.5
Tricyclo-paraffins	0.2	0.2	0.4	<0.1	<0.1	<0.1	0.1	0.1	<0.1	1.3
Alkyl-benzenes	11.7	16.0	11.5	15.2	14.6	17.5	8.7	11.3	10.5	14.7
Tetralins + indans	5.3	7.9	4.4	2.5	4.3	4.1	4.1	5.7	8.9	13.3
Naphthalenes	3.0	1.4	2.3	2.4	1.5	1.7	1.8	1.8	0.3	0.6
Totals[3]	99.9	100	100.4	100.1	99.9	100.1	100.4	100.1	99.7	99.8
Total cyclo-paraffins	30.5	39.4	38.1	28.3	40.8	26.3	40.2	33.8	37.9	31.6
Total aromatics	20.2	25.3	18.2	20.1	20.4	23.3	14.6	18.8	19.7	28.0
(Tet.+Ind.)/arom.[4]	26%	31%	24%	12%	21%	18%	18%	30%	45%	48%

Notes: 1. ARA ReadiJet, 100%
2. KiOR 30/70 blend HDCJ/JP-8
3. Totals not equal to 100 are due to round-off errors
4. % of aromatic fraction that is tetralins + indans

The composition data for the base JP-8 fuels of Table 5 show that the tetralins and indans range from 12% to 31% of the aromatic fraction. Despite this, the fuels are well correlated with a

simple aromatic content. This is supported by the data from 100% ARA ReadiJet and the 30/70 blend of the KiOR HDCJ in JP-8 in which tetralins plus indans make up 45% and 48% of the aromatic fraction. The other renewable fuels added to these figures did not contain synthesized aromatics.

There has been some concern expressed about the possible effect of cyclo-paraffins on volume swell with nitrile materials. The concentration of cyclo-paraffins varied from 26 to 40% of the base fuels and the two renewable fuels. It would appear that such concentrations of cycloparaffins do not significantly affect the volume swell in these data sets so as to upset a simple aromatic correlation in both conventional fuels and fuels containing synthesized hydrocarbons.

4.1.5   Summary of Fuel Effects on Fuel System Elastomers

The results of the evaluations by Graham et al demonstrate that volume swell, the most sensitive property, is linear with aromatic content for all of the materials tested; nitrile materials were the most sensitive to aromatic content. Furthermore, there was very little scatter in these data sets over the range of 0 to 25% aromatics. A review of the hydrocarbon analyses of these fuels, conventional and synthesized, by GCxGC shows that significant fractions of cyclo-paraffins, tetralins, and indans did not affect a simple correlation model with aromatics by ASTM D1319.

4.2   Summary

4.2.1   Tests Considered

This report summarizes the results of two sets of data on fuel effects on fuel system elastomers, i.e., coatings, sealants, and O-rings:

1. The various material compatibility tests performed in conjunction with the individual fuel approvals.
2. The results from a study of the effect of aromatic content on volume swell of various fuel-system elastomeric materials.

A third set of data looking at the effects synthesized fuels on properties of O-rings exists, but was not included in this evaluation because the fuel exposures were done at ambient conditions by different laboratories, with no assurance that the materials, themselves, came from the same batch. Also, the properties evaluated were not always the same from fuel to fuel. Since these materials and properties were all a part of both data sets, i.e., the first data set listed above in which the environmental conditions were more typical of service use and the second data set at ambient temperatures, it was decided that there was little value in including them in this report.

4.2.2   Fuel Effects on Material Properties

The first evaluation consisted of 18 synthesized fuels and blends with conventional jet fuels. The materials and properties were from the "short-short" list and the data were taken from the technical reports of the individual fuels. The materials were coatings, sealants, and O-rings. The property tests, environmental conditions, and technical performance requirements of the materials were those identified in ASTM D4054. The fuels included all types of synthesized products and blends, including those with synthesized aromatics:

- Fischer-Tropsch paraffinic products, i.e., Annex 1
- HEFA products, i.e., Annex 2

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- 2nd generation renewable products from multiple resources and processes, i.e., Annexes 3 and 5 plus other fuels that have not yet gained final approval
- Fischer-Tropsch product with aromatics, i.e., Annex 4
- Fully synthetic fuel from Fischer-Tropsch syn-crude

There were no significant differences in the results whether the materials were exposed to synthesized fuels and blends or conventional fuels of similar aromatic content. Furthermore, the response to synthesized aromatics was the same as the response to conventional aromatics.

4.2.3   Effects of Aromatics on Volume Swell of O-Rings

The effect of aromatics on volume swell of O-rings and sealants was shown to be linear with very little scatter. There was no apparent effect of fuels on volume swell for the coatings. The response to aromatic content for the fuels blended with an F-T fuel was the same as with the conventional jet fuels.

The 3 O-ring materials were the only materials for which there were equivalent data on renewable fuels from the same laboratory. Three of the eight conventional fuels had more than 39 mass% cycloparaffins; seven of the eight fuels had between 4.1 and 7.9 mass% tetralins plus indans. The results of exposure to these fuels fit the same linear model with aromatics by ASTM D1319 as those with lower concentrations. Two of the renewable fuels contained synthesized aromatics and significant levels of cyclo-paraffins and tetralins plus indans. The data for these two fuels also fit the model for conventional fuels and their blends with F-T fuels based simply on D1319 aromatic content.

5.0 CONCLUSIONS

Hydrocarbons don't know where they came from. Therefore, if the synthesized kerosene and blends with conventional jet fuel have a hydrocarbon composition that is within the scope of conventional jet fuel, i.e., 8 to 25 vol%, and any reactive organics or trace contaminants are controlled, any effect of the fuel on the elastomer will be typical of a conventional jet fuel with the same aromatic content. Reactive species are controlled the requirement of passing a JFTOT test at 325°C; trace metals are controlled by the Annex. This conclusion is independent of resource or process. The conclusion also holds for kerosenes containing synthesized aromatics providing the aromatics are well distributed across the boiling range. Control of aromatic content by ASTM D1319 appears to be adequate for the final fuel, although there may be limitations required on cyclo-aromatics, i.e., tetralins and indans, to assure the synthesized product has a composition that is typical of experience with conventional jet fuel.

6.0 RECOMMENDATIONS

It is recommended that consideration be given to the development of a generic Annex to ASTM D7566 that allows for the acceptance of synthesized hydrocarbon kerosenes regardless of resource or processing providing the product has chemistry and boiling range characteristics typical of experience with conventional jet fuel following the guidelines established in Annexes 1, 2, and 4. That is, the hydrocarbons are distributed over at least four significant carbon numbers and the synthesized product passes a JFTOT test at 325°C to control reactive species. If synthesized aromatics are present, they should be distributed over the boiling range. Although alkyl benzenes are preferred, the presence of tetralins and indans would be acceptable if the concentrations are typical of conventional jet fuel. Other issues with properties and trace contaminants would be controlled by Tables Ax.1 and Ax.2 of the Annex in ASTM D7566 as they are currently controlled.

7.0 REFERENCES

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4. Evaluations of Bio-Derived Synthetic Paraffinic Kerosenes (Bio-SPKs), ASTM Report D02-1739 v5.0, May 2010.
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9. GCxGC analyses of test fuels provided by Tim Edwards to the author by email on November 21, 2011.
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11. Graham, J., Minus, D., "Small-Sample Test Methods for Assessing the Compatibility Of Alternative Fuels with Polymeric Materials," Proceedings of the SAMPE 2013 Conference & Exhibition, Long Beach, CA, May 6-9, 2013.
12. Tim Edwards, et al, "Evaluation of Hydroprocessed Depolymerized Cellulosic Jet (HDCJ) Fuels and Blends," Final report on KiOR HDCJ Synthesized Kerosene, KiOR, Inc., Pasadena, TX, April 2014.

List of Symbols, Abbreviations, and Acronyms

<u>Acronym</u>	<u>Description</u>
AFRL	Air Force Research Laboratory
APFEERD	Airbreathing Propulsion Fuels and Energy Exploratory Research and Development
ATJ	Alcohol to Jet
CAAFI	Commercial Aviation Alternate Fuels Initiative
CH	Catalytic Hydrothermolysis
CRC	Coordinating Research Council
DoD	Department of Defense
FSJF	Sasol Fully Synthetic Jet Fuel
F-T	Fischer-Tropsch
HDCJ	Hydrotreated Depolymerized Cellulosic Jet
HEFA	Hydrotreated Esters and Fatty Acids
IPK	Iso-Paraffinic Kerosene
OEM	Original Equipment Manufacturer
R4RQ	Research for the Aerospace Systems Directorate
RQ	Aerospace Systems Directorate
RQT	Turbine Engine Division
RQTF	Fuels and Energy Branch
SPK	Synthesized Paraffinic Kerosenes
UDRI	University of Dayton Research Institute
USAF	United States Air Force
UTC	Universal Technology Corporation
WPAFB	Wright-Patterson Air Force Base